# **Friction Properties of Vegetable Oils**

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**ABSTRACT:** Vegetable oils are a renewable and an environmentally friendly alternative to petroleum-based oils in lubrication and other important application areas. Vegetable oils fall into two broad chemical categories: triesters (or TG) and monoesters. Most vegetable oils are triesters of glycerol with FA, whose characteristics are dependent on the chemistry and composition of the FA residues. A small percentage of vegetable oils are monoesters of long-chain FA and fatty alcohols of varying chemistries. In this work, the free energy of adsorption ( $\Delta G_{\rm ads}$ ) of safflower (SA), high-oleic safflower (HOSA), and jojoba (JO), methyl oleate (MO), and methyl palmitate (MP) on steel were investigated. SA and HOSA are TG of vegetable oils with FA residues of radically different degrees of unsaturation. JO is a monoester vegetable oil.  $\Delta G_{\rm ads}$  is one of the major factors affecting the boundary friction properties of lubricant ingredients.  $\Delta G_{\rm ads}$  was found to increase in the order: HOSA  $\leq$  SA < JO < $MO \leq MP$ . The results are consistent with the degree of functionality and other chemical properties of the oils studied.

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Vegetable oils are obtained from renewable agricultural sources (1,2). They are also nontoxic and have excellent environmental and safety characteristics. These properties make vegetable oils attractive alternatives to petroleum-based oils in lubrication and other applications (1–5).

Vegetable oils can be grouped into two broad chemical categories (2). Most vegetable oils are triesters of glycerol with various types of FA and are commonly referred to as TG. A few vegetable oils are monoesters of long-chain FA and fatty alcohols of varying degrees of unsaturation.

Most vegetable oils can be considered to be amphiphilic since they comprise distinctly separated regions of polar and nonpolar groups in the same molecule. The polar groups constitute at least one ester functional group. The nonpolar groups are hydrocarbons of varying chain lengths, degrees of unsaturation, and stereochemistry. Depending on the type of vegetable oil, functional groups such as epoxides and hydroxides may be present in the hydrocarbon portion of the mole-

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cule. The tribological and other properties of vegetable oils are highly dependent on the exact chemical composition of its polar and nonpolar groups. For example, a TG with a lower degree of unsaturation will have better oxidative stability than a TG with a higher degree of unsaturation (6–8).

Most vegetable oils are considered functional fluids since they have at least one functional group (an ester) and are also liquid at room temperature. This property allows vegetable oils to be used in lubricant formulations as base oils and/or boundary additives. Most lubrication processes occur in one of three lubrication regimes: boundary, hydrodynamic, and mixed (9). Vegetable oils, being functional fluids, can be used in all three regimes. However, successful application of vegetable oils in lubricant formulations requires understanding the effect of vegetable oil chemistry on both their fluid and boundary properties.

Two factors that affect the boundary lubrication properties of vegetable oils are adsorption and reaction (9–19). Adsorption refers to the ability of the oil to adsorb onto friction surfaces and prevent their contact during a tribological process. Adsorption occurs mainly due to the interaction of the functional groups of the vegetable oils with the friction surfaces and can be quantified using free energy of adsorption ( $\Delta G_{ads}$ ) terms. Reaction deals with the tendency of the vegetable oils to undergo chemical reaction by themselves or with other materials (e.g., oxygen, moisture, metal) in the interface or friction zone. Reaction occurs owing to the high temperature, pressure, and shear of the lubrication process. These reactions, called tribochemical reactions, are poorly understood and are responsible for a number of phenomena such as degradation of the oil due to oxidation and the generation of friction polymers. Successful application of vegetable oils in lubrication requires a thorough understanding of these tribochemical phenomena.

In this work, the effect of the chemical properties of a vegetable oil on its  $\Delta G_{\rm ads}$  on steel was investigated. One monoester and two triester vegetable oils along with methyl palmitate (MP) and methyl oleate (MO) were used. The monoester vegetable oil was jojoba (JO), which comprises unsaturated long-chain FA and fatty alcohol residues (5,20). The two triester vegetable oils were safflower oil (SA) and high-oleic safflower oil (HOSA), both of which are obtained from naturally occurring safflower plants. HOSA is obtained from safflower plants that produce more oleic than linoleic acid residues (1). SA and HOSA comprise oleic to linoleic FA residues of 18:73 and 78:13, respectively. Since oleic and linoleic acids have one and two double bonds, respectively, SA will have a dramatically higher degree of unsaturation

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than HOSA. This difference in the degree of unsaturation has been shown to result in a dramatically improved oxidative stability of HOSA over SA (7,8).

 $\Delta G_{\rm ads}$  was obtained from the analysis of friction-derived adsorption isotherms of the oils on steel using the Langmuir (21) and Temkin (22) models. The friction-derived adsorption isotherms were obtained from boundary friction measurements using the method of Jahanmir and Beltzer (10).

The  $\Delta G_{\rm ads}$  of adsorbates such as vegetable oils are highly dependent on the chemistries of both their polar and non-polar groups (10–16). The vegetable oils used in this study varied in the number of functional groups, chain length, and degree of unsaturation. This paper describes our study on the effect of these chemical variations on  $\Delta G_{\rm ads}$  of vegetable oils.

## **MATERIALS AND METHODS**

Lubricants. All lubricant ingredients were obtained commercially and used as supplied. Lubricant formulations comprised two ingredients: a base oil, which was hexadecane (99+% anhyd; Aldrich Chemical Company, Milwaukee, WI) and one of the following additives: SA (Liberty Vegetable Oil Co., Santa Fe Springs, CA); HOSA (Oilseeds Intl. Ltd., San Francisco, CA); JO (USDA, Peoria, IL); MO and MP (99+%, Sigma, St. Louis, MO). The lubricant formulations contained 0.003 to 0.6 M of each additive in hexadecane.

Friction measurement. Friction was measured as described previously (23) under point contact conditions, using a ball-ondisk configuration on a Falex Friction & Wear Test Machine, Model Multi-Specimen (Falex Corporation, Sugar Grove, IL). The balls and disks (Falex Corporation) were thoroughly degreased by consecutive sonications in fresh reagent-grade isopropyl alcohol (Aldrich Chemical Company) and hexane (Aldrich Chemical Company) prior to use. The specifications of the balls were: 52100 steel; 12.7 mm (0.5 in.) diameter; 64-66 Rc hardness; extreme polish. The specifications of the disks were: 1018 steel; 25.4 mm (1 in.) o.d.; 15–25 Rc hardness;  $0.36-0.46 \mu m$  (14–18  $\mu in.$ ) roughness. The instrument is capable of automatic acquisition and display of friction force, wear, load, speed, and lubricant/specimen temperature at a rate of 1/s. During the test, the coefficient of friction (COF) was automatically calculated and displayed in real time. Data were also saved on a computer disk for further analysis.

Friction measurement setup. In the ball-on-disk configuration of the Falex Multi-Specimen tester, the ball and disk are fixed on the upper and lower specimen holders, respectively, with a point contact radius of 11.9 mm (0.468 in.) (23). The bottom specimen holder is placed in an enclosed cup, containing 50 mL of lubricant in which the ball-and-disk assembly are completely immersed. At the start of the test, the disk assembly is raised and made to contact the ball. The ball is then allowed to rotate and, as soon as it reaches the set speed, application of the load begins and gradually increases until it reaches the set value. The friction measurement continues until the set time elapses. A second test is conducted using the lubricant sample from the first test with a new set of ball

and disk specimens. The COF from the duplicate tests are then averaged to obtain the COF of the lubricant being tested. In general, the SD of the COF from the duplicate runs was less than  $\pm 5\%$  of the mean.

Friction measurements were conducted at room temperature, for 15 min, at 6.22 mm/s (5 rpm) and a 181.44-kg (400 lb) load. The temperature of the specimen and lubricant at the start of the test was  $25 \pm 2^{\circ}$ C. This temperature increased by  $1-2^{\circ}$ C during the 15-min test period.

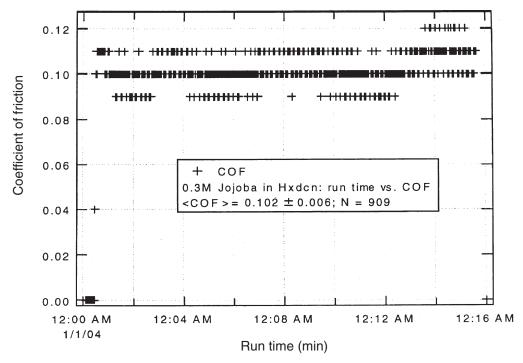
#### **RESULTS AND DISCUSSION**

Boundary friction measurement. The boundary COF of twocomponent lubricant formulations were measured at 6.22 mm/s speed and 400 lb load using the ball-on-disk geometry (23). The lubricant formulations consisted of a base oil, which was hexadecane, and one of the following additives dissolved in hexadecane: SA, HOSA, JO, MP, MO. Several concentrations of each additive ranging from 0.00 to 0.60 M were used. In a typical procedure, the disk is immersed in the lubricant contained in a cup. The ball is then pressed against the disk with the specified load and rotated at the specified speed. The COF is recorded as a function of time for the duration of the test, which was 15 min. At the end of the test, a new disk and ball set was installed and a repeat test performed on the same lubricant formulation. All tests were conducted at room temperature (25  $\pm$  2°C). The temperature of the lubricant was monitored during each test and showed a slight increase of less than 2°C after the 15-min test.

A typical time vs. COF output from such measurement is shown in Figure 1. The COF data in the steady-state region were averaged to calculate the COF for each run. COF values from repeat runs were within 5% of each other. These were averaged to obtain the COF of the lubricant formulation, which was then used in subsequent analyses.

Friction-based adsorption isotherms. The effect of additive concentration in hexadecane on COF is illustrated in Figure 2. All the additives studied in this work showed similar profiles, with three main features: (i) a region of very high COF corresponding to very low additive concentration; (ii) a region of very sharp decrease in COF with increasing additive concentration; and (iii) a region where the COF was independent of the additive concentration. These COF values are reflections of the surface concentration of the additives at the steel surface, which is a function of the additive concentrations in hexadecane. At low additive concentrations, the surfaces are almost exclusively covered with hexadecane, and the COF will be close to that of pure hexadecane, which is ~0.5 (23). As the concentration of additive in hexadecane increases, so does its surface concentration, resulting in a dramatic decrease in COF. At very high concentration of additive in hexadecane, the surface is almost completely covered with the additive, and the COF becomes independent of the concentration of additive in hexadecane.

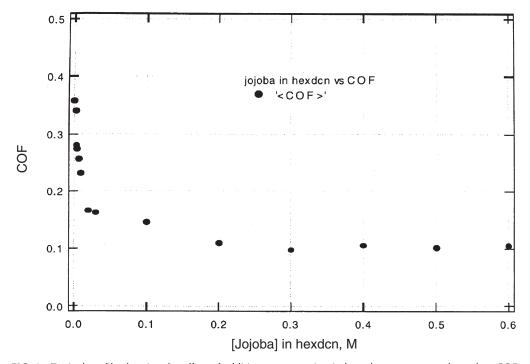
An adsorption isotherm shows the relationship between the concentration of a solute in a solution and that on a sur-



**FIG. 1.** Typical run time vs. coefficient of friction (COF) plot of a ball-on-disk geometry on a Falex Multi-Specimen tester (Falex Corp., Sugar Grove, IL). Hxdcn, hexadecane.

face (24). Various methods are available for constructing adsorption isotherms (24). In this work, adsorption isotherms were obtained from the relationship between the boundary COF of a solute and its solution concentration, following the method of Jahanmir and Beltzer (10). We will refer to these adsorption isotherms as friction-derived adsorption isotherms.

Jahanmir and Beltzer (10) showed that friction-derived adsorption isotherms could be constructed from boundary COF vs. concentration data, provided certain stringent conditions are met. These include: (i) adsorption of the solute from the solution to the friction surfaces must occur *via* a reversible equilibrium for the duration of the friction test, and (ii) the observed



**FIG. 2.** Typical profile showing the effect of additive concentration in hexadecane on mean boundary COF. For abbreviations see Figure 1.

boundary friction must be due to the adsorption of the solute being tested but not to other tribospecies generated during the test. Thus, for example, this method cannot be used for solutes that hydrolyze, decompose, oxidize, polymerize, etc. during the test. The method also cannot be used for solutes that react with the friction surfaces under the test conditions (e.g., extreme pressure additives) and that generate new species *in situ*.

For solutes that meet the stringent conditions discussed above, Jahanmir and Beltzer (10) give the following equation for constructing friction-derived adsorption isotherms from boundary COF vs. concentration data:

$$\theta = \theta_a = (f_b - f)/(f_b - f_a)$$
 [1]

where  $f_b$  is the COF of the pure solvent, which is hexadecane in this work;  $f_a$  is COF at full coverage of the surface by the solute, which are the additives in this work; and  $\theta$  is the concentration of the solute on the surface expressed in terms of fractional surface coverage.  $\theta$  has values ranging from 0.0 at no surface coverage, i.e., at  $f = f_b$ , to 1.0 at full surface coverage, i.e., at  $f = f_a$ . Detailed derivation of Equation 1 is given elsewhere (10).

The concentration vs. COF data obtained in this work were used to determine the COF at full surface coverage ( $f_a$  in Eq. 1) for the various additives used in this work. Table 1 summarizes these  $f_a$  values and also the  $f_b$  value for hexadecane. The COF values of the oils at different concentrations (f in Eq. 1) along with the  $f_a$  and  $f_b$  values of Table 1 were used to calculate the fractional surface coverage,  $\theta$ , values using Equation 1. Typical friction-derived adsorption isotherms, i.e., concentration in hexadecane vs.  $\theta$ , are shown in Figure 3. Also plotted in Figure 3 are the COF data used for calculating the corresponding  $\theta$ . As can be seen in Figure 3, the COF and  $\theta$  values are mirror images of each other. Figure 3 depicts the data for the vegetable oils (JO, SO, HOSO) studied in this work; similar results were observed for the methyl esters (MO, MP) used in this study.

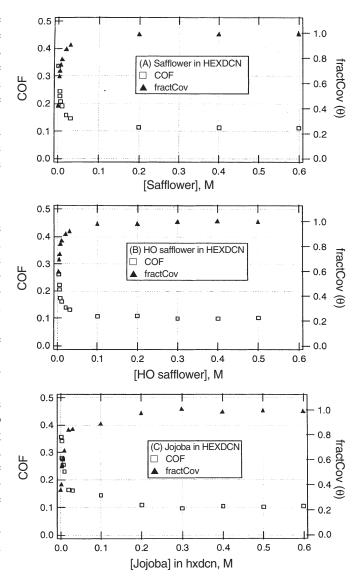
The concentration vs.  $\theta$  data shown in Figure 3 are important because they allow for the determination of the  $\Delta G_{\rm ads}$  of the vegetable oils on steel. This is done by analyzing these friction-derived adsorption isotherms using appropriate adsorption models. Such analysis also gives insight into the interaction of the vegetable oils with steel and with each other.

Estimation of  $\Delta G_{ads}$ .  $\Delta G_{ads}$  is the sum of the free energies due to adhesive or primary interaction between the additive and the surface,  $\Delta G_{o}$ , and lateral interaction between additive molecules (10–15,23):

TABLE 1
Steel/Steel Boundary Coefficient of Friction (COF)<sup>a</sup>

Additive	COF	Additive	COF
None (pure hexadecane)	0.5 <sup>b</sup>	Jojoba	0.10
Safflower	0.11	Methyl oleate	0.13
High-oleic safflower	0.10	Methyl palmitate	0.11

<sup>&</sup>lt;sup>a</sup>Without additives in pure hexadecane ( $f_b$  in Eq. 1), and with full additive surface coverage ( $f_a$  in Eq. 1), obtained on a Falex MS tester using a ball-on-disk geometry.



**FIG. 3.** Friction-derived adsorption isotherms of vegetable oils on steel: (A) safflower oil, (B) high-oleic (HO) safflower oil, and (C) jojoba oil. The fractional surface coverage (fractCov) values are obtained from the COF data using Equation 1. (Note that fractCov in the figure corresponds to  $\theta$  in Eq. 1.) HO, high-oleic. For abbreviations see Figure 1.

$$\Delta G_{\rm ads} = \Delta G_{\rm ads} + \alpha \theta$$
 [2]

where  $\alpha$  is the net free energy of lateral interaction of additives. The net lateral interaction could be attractive ( $\alpha < 0$ ), repulsive ( $\alpha > 0$ ), or inconsequential ( $\alpha \cong 0$ ).

Calculation of  $\Delta G_{\rm ads}$  using Equation 2 requires values for  $\Delta G_{\rm o}$  and  $\alpha$ . These values are obtained from the analysis of the adsorption isotherm data using an appropriate adsorption model. The Langmuir (21) and Temkin (22) adsorption models are used in this work.

In the Langmuir model, lateral interactions are ignored and Equation 2 reduces to:

$$\Delta G_{\rm ads} = \Delta G_{\rm o}$$
 [3]

<sup>&</sup>lt;sup>b</sup>Reference 23.

The Langmuir model predicts the following relationship between fractional surface coverage,  $\theta$ , and solute concentration:

$$\theta = (K_0 C)/(1 + K_0 C)$$
 [4]

where C is the solute concentration (mol/L), and  $K_o$  is the equilibrium constant for the displacement of a solvent molecule from the surface by a solute molecule in solution.  $K_o$  is obtained from the slope of  $1/\theta$  vs. 1/C plot and is used to calculate  $\Delta G_{\rm ads}$  (Eq. 5):

$$\Delta G_{\text{ads}} = \Delta G_{\text{o}} = RT \ln(K_{\text{o}})$$
 [5]

In the Temkin model, a net repulsive lateral interaction is assumed, i.e.,  $\alpha > 0$ . Thus, Equation 2 is used to calculate  $\Delta G_{\rm ads}$ , using  $\Delta G_{\rm o}$  and  $\alpha$  values obtained from a Temkin model. The exact equation of the Temkin model used for estimating  $\Delta G_{\rm o}$  and  $\alpha$  depends on the range of fractional surface coverage being considered. For  $0.2 \le \theta \le 0.8$ , the Temkin model predicts the following relationship between fractional surface coverage,  $\theta$ , and solute concentration (9–14):

$$\theta = (RT/\alpha)\ln(C/K_0)$$
 [6]

Equation 6 predicts a linear relationship between  $\theta$  and  $\ln(C)$ . To determine  $\Delta G_{\rm ads}$  using the Temkin model, the values of  $\alpha$  and  $K_{\rm o}$  are first obtained from the slope and intercept of the  $\ln(C)$  vs.  $\theta$  plot of Equation 6. Then  $\Delta G_{\rm o}$  is obtained using Equation 7:

$$\Delta G_0 = (RT)\ln(K_0)$$
 [7]

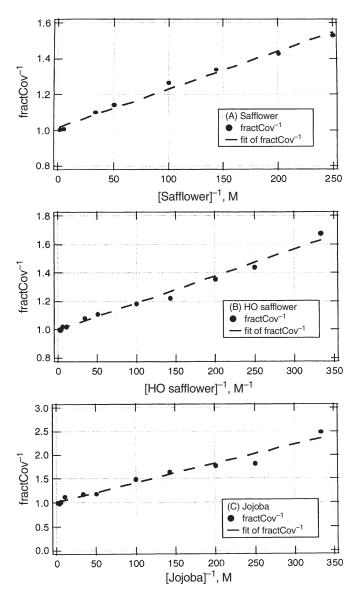
Finally  $\Delta G_{\text{ads}}$  is obtained from Equation 2 at  $\theta = 1$ , i.e.,

$$\Delta G_{\text{ads}} = \Delta G_{0} + \alpha \theta = \Delta G_{0} + \alpha$$
 [8]

Analysis of friction-derived adsorption isotherms. The friction-derived adsorption isotherms shown in Figure 3 were analyzed using the Langmuir and Temkin adsorption models. From these analyses, the  $\Delta G_{\rm ads}$  of the vegetable oils were determined.

The Langmuir adsorption model predicts a linear relationship between the reciprocal of the additive concentrations in hexadecane and the reciprocal of the fractional surface coverage,  $\theta$ , with an intercept of 1.0. Langmuir analysis of the friction-derived adsorption isotherms showed such a linear relationship for all the additives used in this work, with a correlation coefficient of >0.9. Typical results of these analyses are shown in Figure 4.  $K_0$  was obtained from the slopes of such plots and used to calculate  $\Delta G_{\rm ads}$  using Equation 5. Figure 4 depicts the results for the vegetable oils, which were similar to those obtained for the methyl esters.

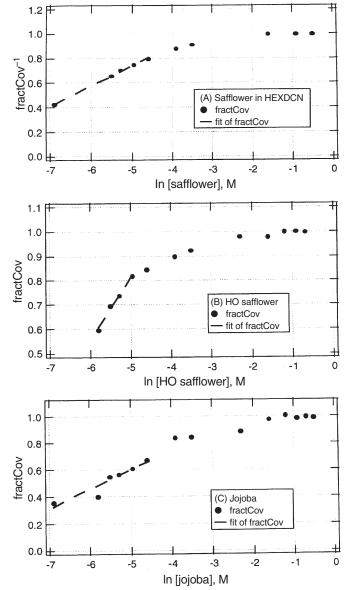
As mentioned earlier, the Temkin adsorption model predicts a linear relationship between the logarithm of the oil concentration in hexadecane and  $\theta$  in the fractional surface coverage range of  $0.2 \le \theta \le 0.8$  (Eq. 6). Temkin analysis of



**FIG. 4.** Langmuir analysis (Eq. 4) of friction-derived adsorption isotherms of vegetable oils: (A) safflower oil, (B) HO safflower oil, and (C) jojoba oil. (Note that fractCov in the figure corresponds to  $\theta$  in Eq. 4.) For abbreviations see Figures 1 and 3.

the friction-derived adsorption isotherm data in this range of fractional surface coverage showed such a linear relationship for all the additives used in this study, with a correlation coefficient of >0.9. Typical results of the Temkin analysis are illustrated in Figure 5. From the slopes and intercepts of such fits,  $\alpha$  and  $K_0$  were obtained and used to calculate  $\Delta G_{\rm ads}$  using Equations 7 and 8. Figure 5 depicts the results for the vegetable oils, which were similar to those obtained for the methyl esters.

The  $\Delta G_{\rm ads}$  of the vegetable oil and methyl ester additives obtained from the Langmuir and Temkin analyses are summarized in Table 2, along with literature (10,11,23)  $\Delta G_{\rm ads}$  data for similar additives obtained from the analysis of friction-derived isotherms.



**FIG. 5.** Temkin analysis (Eq. 6) of friction-derived adsorption isotherms of vegetable oils: (A) safflower oil, (B) HO safflower oil, and (C) jojoba oil. (Note that fractCov in the figure corresponds to  $\theta$  in Eq. 6.) For abbreviations see Figures 1,3.

Comparison of the  $\Delta G_{\rm ads}$  data indicates consistently lower values from the Langmuir than from the Temkin analysis for all the materials used in this work. This is similar to previous results on other vegetable oils and methyl esters (23). These differences in  $\Delta G_{\rm ads}$  values are a reflection of the differences in the basic assumptions of the Langmuir and Temkin models. The Langmuir model ignores lateral interaction, whereas the Temkin model assumes a net repulsive, i.e., positive, lateral interaction. Inclusion of lateral interaction will result in a higher  $\Delta G_{\rm ads}$  value (smaller negative number) from the Temkin model.

Comparison of the  $\Delta G_{\rm ads}$  data for the triester vs. the monoester additives used in this study shows that both models predict the lowest  $\Delta G_{\rm ads}$  values (strongest adsorption onto steel surfaces) for the triesters HOSA and SA. Similar results were obtained in previous studies on TG and monoesters and were

attributed to multiple adhesive interactions between the TG and the steel surface (23).

HOSA contains a high amount of oleic acid (with only one double bond), whereas SA has an overabundance of linoleic acid (with two double bonds). Consideration of Table 2 with respect to TG unsaturation shows that the  $\Delta G_{\rm ads}$  value of HOSA is similar to or slightly lower than that of SO. This result is independent of the model used to calculate the  $\Delta G_{\rm ads}$  values. Similar results were obtained in a previous comparative study on normal and high-oleic soybean oils (23). It appears that the radical difference in the degree of unsaturation between SO and HOSO had a minor effect on their adsorption properties.

Comparison of  $\Delta G_{\rm ads}$  values of the triester and monoester additives used in this study shows that the two models give different trends. The Langmuir model predicts  $\Delta G_{\rm ads}$  increasing in the order HOSA  $\leq$  SA < JO < MO  $\leq$  MP, whereas the Temkin model predicts  $\Delta G_{\rm ads}$  increasing in the order HOSA < SA < MP < JO << MO. The trend from the Langmuir analysis is consistent with expectations based on the effects of degree of functionality and chain lengths of the additives.

Comparison of the  $\Delta G_{\rm ads}$  values of the monoesters used in this work shows that the Langmuir model predicts the lowest  $\Delta G_{\rm ads}$  value for JO, whereas the Temkin model predicts MO to have the lowest  $\Delta G_{\rm ads}$  value. Also, the two models predict different trends in the  $\Delta G_{\rm ads}$  values of the monoesters. Comparison of the trends from the two models indicates that the trend predicted by the Langmuir model is consistent with expectations based on the effects of chain length on adsorption. The observed  $\Delta G_{\rm ads}$  values decrease with increasing chain length. Longer chains result in stronger dispersive interactions of the hydrocarbon chains, which will contribute to attractive interactions between the oil and the surface.

Data for the  $\Delta G_{\rm ads}$  values of normal and high-oleic TG from two different plant varieties—safflower and soybean (23)—indicate that the Langmuir model gives almost identical  $\Delta G_{\rm ads}$  values for the normal and for the high-oleic oils from these two plant varieties (Table 2). The Temkin model also gave identical values for the normal SA and soybean oils. However, it gave slightly different values of  $\Delta G_{\rm ads}$  for the high-oleic SA and soybean oil. The observed similarities in the  $\Delta G_{\rm ads}$  values of the oils from these two plant varieties could be due to the similarities in the chemical compositions of soybean and SA oils (3).

Comparison of adsorption models. The resulting  $\Delta G_{\rm ads}$  values are highly model dependent. In general, the Langmuir model predicts a stronger adsorption (more negative  $\Delta G_{\rm ads}$  values) than the Temkin model. This result is consistent with the basic assumptions of these two models, i.e., the Temkin models assumes a net repulsive lateral interaction and the Langmuir model ignores lateral interactions. The result will be larger (less negative)  $\Delta G_{\rm ads}$  values from the Temkin than from the Langmuir model.

Both models showed improved adsorptions by TG over monoesters, which was attributed to multifunctional interactions between TG and the steel surface.

TABLE 2 Free Energies of Adsorption,  $\Delta G_{ads'}$  of Selected Lubricant Additives<sup>a</sup>

	Friction surfaces		$\Delta G_{ m ads}$ (kcal/mol)		
Lubricant additive $^b$		Test geometry	Langmuir	Temkin	Reference
HO safflower	Steel/steel	Ball-on-disk	-3.71	-2.53	c
Safflower	Steel/steel	Ball-on-disk	-3.65	-2.01	c
HO soybean oil	Steel/steel	Ball-on-disk	-3.7	-2.1	23
Soybean oil	Steel/steel	Ball-on-disk	-3.6	-2.1	23
Jojoba	Steel/steel	Ball-on-disk	-3.27	-1.31	С
Methyl oleate	Steel/steel	Ball-on-disk	-2.91	-1.02	c
Methyl palmitate	Steel/steel	Ball-on-disk	-2.70	-1.63	c
Methyl laurate	Steel/steel	Ball-on-disk	-1.9	-0.6	23
Methyl oleate	Cu/Cu	Ball-on-cylinder		-1.3	10
Methyl stearate	Cu/Cu	Ball-on-cylinder		-1.3	10
Methyl stearate	Steel/steel	Four-ball		-2.5	11
Ethyl stearate	Steel/steel	Four-ball		-3.0	11

<sup>a</sup>Obtained from the analysis of friction-derived adsorption isotherms using the Langmuir and Temkin adsorption models. The friction-derived adsorption isotherms used in the analysis were obtained from boundary COF measurements between the indicated friction surfaces, using the indicated test geometries.

Both models also showed zero or very small effect on the  $\Delta G_{\rm ads}$  of TG due to changes in the degree of unsaturation. Similar results have been reported on another TG vegetable oil (23). This observation indicates that the effect on lateral interaction due to unsaturation is too small to affect the  $\Delta G_{\rm ads}$  of vegetable oils. High-oleic vegetable oils are preferred ingredients in lubricant formulation due to their lower degree of unsaturation, and, hence, better oxidative stability relative to normal vegetable oils. The results of this study indicate that replacing normal TG vegetable oils with high-oleic TG vegetable oils in lubricant formulations will result in improved oxidative stability without impairing the boundary lubrication properties of the lubricant.

The Langmuir model gave identical values of  $\Delta G_{\rm ads}$  for normal TG vegetable oils from two different plant species—safflower and soybean. It also gave similar results for high-oleic TG vegetable oils from these two plant species. The Temkin model also gave similar results on both normal and high-oleic TG vegetable oils from these two plant species. This observation was attributed to the similarities in the chemical compositions of the oils from these two plant species.

The Langmuir and Temkin models gave different trends in the effects of chain length on the  $\Delta G_{\rm ads}$ . However, the trends predicted by the Langmuir model were consistent with expectations based on the effect of chain dispersion interactions on adsorption. Also, in the analysis of the effect of unsaturation on  $\Delta G_{\rm ads}$ , both models showed no effect. The ratio of oleic to linoleic acid residues of SO and HOSO are 18:73 and 78:13, respectively. Such a high degree of unsaturation in SO relative to HOSO was expected to lead to major differences in lateral interactions, which should show up in a Temkin analysis of the data. The fact that the Temkin analysis showed no such differences might be an indication that lateral interactions cancel each other out resulting in a net lateral interaction that is too

small to interfere with the primary adhesive interaction between the TG and the steel surface. If this is the case, it will be appropriate to analyze the fractional coverage data of TG using the Langmuir rather than the Temkin isotherm. The Langmuir isotherm is derived for systems that do not involve lateral interactions and is also suitable for analyzing systems in which attractive and repulsive lateral interactions cancel out resulting in very small or zero net lateral interaction. These observations support the conclusion that the Langmuir model is better suited for the estimation of the  $\Delta G_{\rm ads}$  of vegetable oils.

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